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Permeability of
Portland Cement Paste

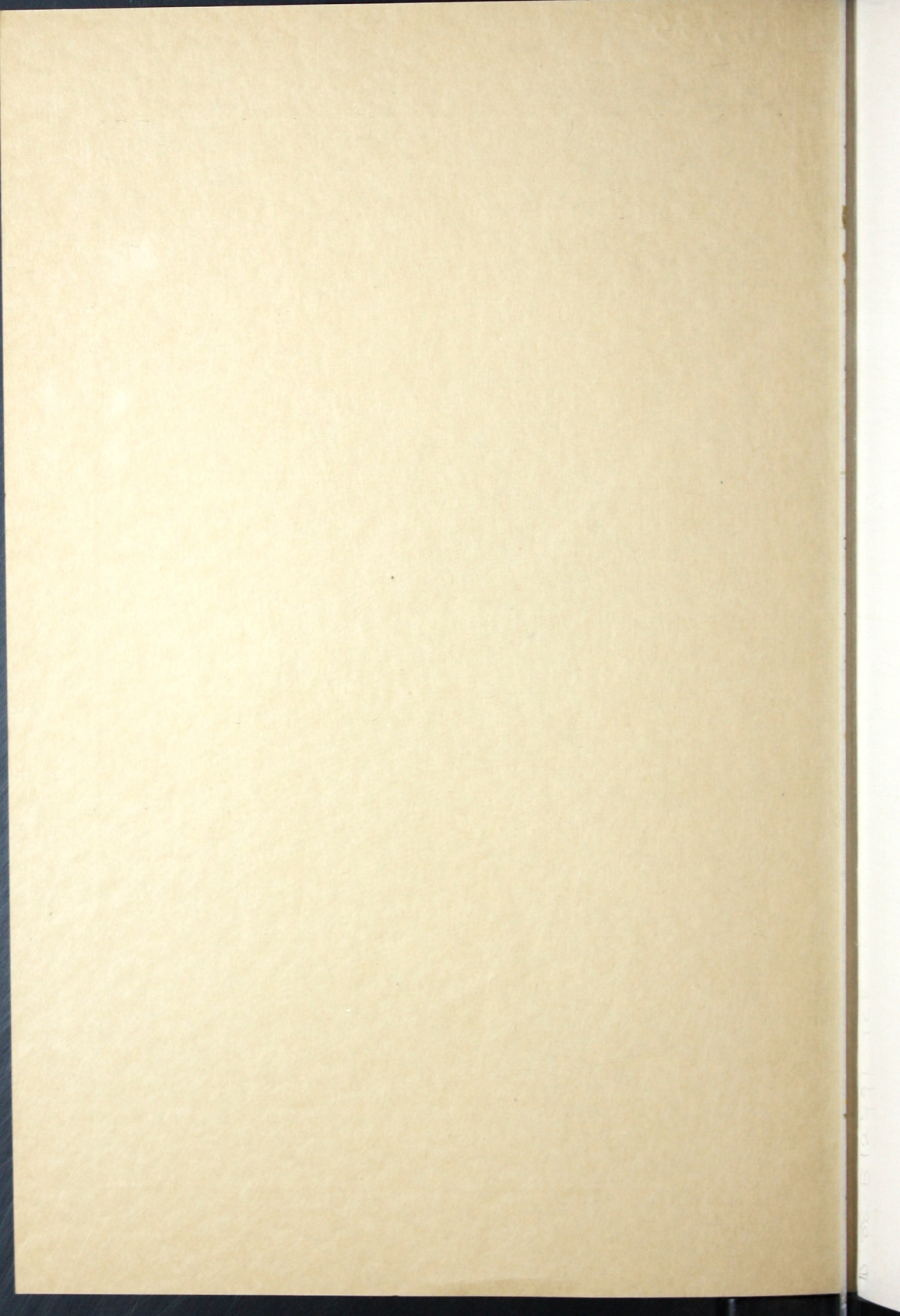
BY

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Permeability of Portland Cement Paste*

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SYNOPSIS

Apparatus and methods for measuring the permeability of portland cement pastes are described. Test results are given showing the effects of curing, cement content, cement composition, and cement fineness. Also, data on some rocks are compared with data on hardened pastes.

INTRODUCTION

This paper deals with experiments on the permeability to water of portland cement paste. The relationship of the permeability of the paste to that of concrete as a whole is understood in a general way. The paste is a continuous body enveloping and isolating the individual aggregate particles. The over-all permeability is a function of the paste permeability, the permeability of the aggregate particles, and the relative proportions of the two. Fissures under the aggregate particles formed during the period of bleeding, and cracks caused by volume-change restraint also play a part. The permeability of paste has also an important bearing on the vulnerability of concrete to frost action. It determines the relative ease with which the cement paste and the aggregate may become resaturated after drying, and it is a principal factor determining the destructiveness of freezing—once the paste becomes water-soaked. This latter subject has been treated extensively in other papers.^{1,2,3} Studies of paste permeability have thrown light on the question of hydrostatic pressure in the interior of dams. Along with other information they have helped to identify the "ultimate particles" against which hydraulic forces inside the concrete can develop. With these particles identified and their wettable areas measured, the order of magnitude of the area factor for computing hydrostatic uplift forces within concrete dams could be established.⁴

EXPERIMENTAL METHODS

The apparatus used for permeability measurements is shown schematically in Fig. 1, and its actual appearance in Fig. 2. Fig. 1 shows the system in which hydrostatic pressure is produced by standpipes of mercury, and it shows one of the four permeability cells attached to that system.

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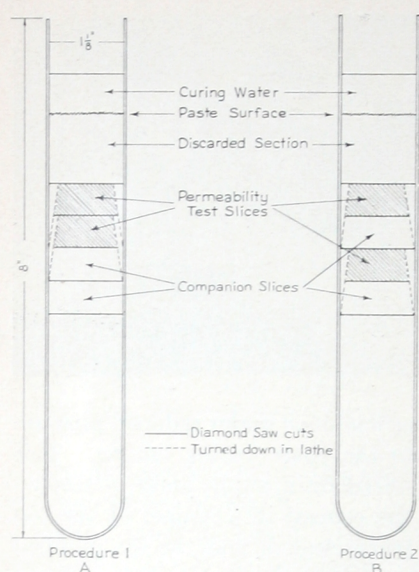


Fig. 4—Relative size and position of test slices with respect to the original specimen

density below which the density increases with distance from the top. These are the normal effects of sedimentation, as discussed in a previous publication.⁵

In a sample such as that shown in Fig. 5, slices cut from the zone of constant density would be comparatively homogeneous and the specimens for permeability tests would have the same composition as those used for auxiliary tests. However, if the slices had been cut from the lower zone, the specimens would not be isotropic and the companion pieces would not be like the permeability pieces.

The pattern shown in Fig. 5 does not represent all samples; the depth of the zone of constant density varies from paste to paste and in some cases the density varies continuously from top to bottom. Procedure 2, as illustrated in Fig. 4, was adopted to reduce the difference between permeability samples and their companions.

In all recent work the auxiliary tests were made on the permeability sample after completion of the permeability test. The auxiliary tests referred to were principally those required to determine the total water content and the nonevaporable water content.*⁶ Also, the densities (specific gravities) were measured prior to determining the water contents.

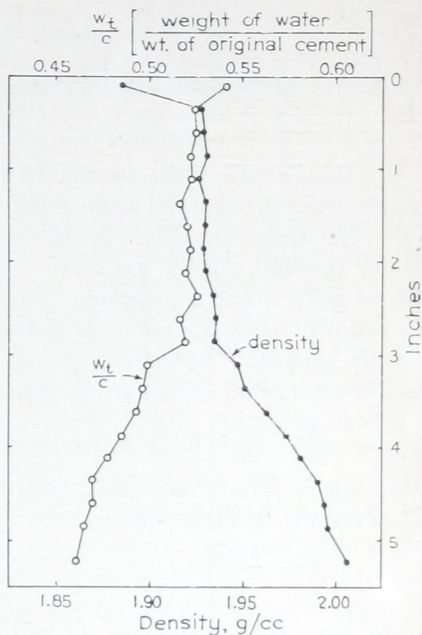
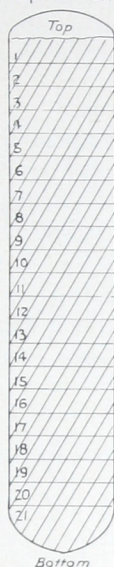
At high water contents, the pastes tend to develop vertical channels during the bleeding period.⁵ Such channels probably do not become completely filled with hydration products. The procedure described above did not eliminate this fault. Although the channels were not visible, we believe they might have been present in some specimens and might account for what seems to be abnormally high coefficients of permeability.

Early in these investigations preheating of the cement was used to induce

*The nonevaporable water is practically equal to the chemically combined water.

Fig. 5—Total water and density versus distance from top of specimen

Diagram of Specimen



false set and thus to produce uniformity of density with depth in a molded specimen. Upon observing that this treatment also resulted in an increased permeability, the preheating was discontinued. With three exceptions the data in this paper were obtained entirely from investigations on specimens prepared without preheating the cement. The exceptions are: (1) Table 2—Effect of Hydration; (2) Table 4—Effect of Cement Fineness; and (3) Table 5—Effect of Drying. We believe that each of these factors would have the same influence, regardless of whether or not the cement had been preheated.

Method of measuring rate of flow

In most tests the samples were placed in the permeability cells, subjected to a constant hydrostatic pressure of about 3 atmospheres, and kept under observation until a steady state of flow was closely approximated. Sometimes the flow rate would become practically constant within 3 or 4 days, but often the required period was as long as 4 weeks. During the period of observation the rate of flow was measured at least once a day by making four or five readings.

Calculation of coefficient of permeability

The fundamental definition of the coefficient of permeability may be stated as follows, using Muskat's development⁷ and the nomenclature of a previous paper.⁸

$$\frac{dq}{dt} \times \frac{1}{A} = \frac{K_2}{\eta} \times \frac{\Delta P}{L} \dots \dots \dots (1)$$

where dq/dt = rate of flow in cu cm per sec

A = mean cross-sectional area of sample, sq cm

η = viscosity of water at the temperature of the experiment

ΔP = pressure drop across specimen, dynes per sq cm

L = thickness of sample, cm

K_2 = coefficient of permeability, sq cm

By this definition the coefficient of permeability is a property of the paste alone; theoretically, the same result would be obtained with different liquids by using their respective coefficients of viscosity η . However, for flow of water through cement paste we have reason to believe that the coefficient of viscosity is not a constant. When water flows through channels as small as those in cement paste, the viscosity appears to be a function of the size of the channel. Therefore, for our present purpose, it is advantageous to use the following definition of permeability coefficient:

$$\frac{dq}{dt} \times \frac{1}{A} = K_1 \frac{\Delta h}{L} \dots \dots \dots (2)$$

Here Δh = drop in hydraulic head across specimen and K_1 is in cm per sec. It is related to K_2 as follows:

$$K_1 = \frac{K_2 d_f g}{\eta_e}$$

where d_f = density of the fluid, g per cu cm

g = acceleration due to gravity, cm per sec per sec

η_e = effective viscosity, poises

It thus embodies the properties of the solid and the liquid, whatever may be the manner and degree to which their properties may be altered by physical interaction. When K_2 is calculated on the basis of $\eta_e = 0.0085$ poise,

$$K_1 = 1.15 \times 10^5 K_2 \dots \dots \dots (3)$$

Neither Eq. (1) nor Eq. (2) applies exactly to flow through a truncated cone, which is the shape of these test specimens. An exact equation for the flow through a body so shaped cannot be obtained. We used Eq. (2) with A calculated from

$$A = \frac{\pi}{8} (d_1^2 + d_2^2) \dots \dots \dots (4)$$

where A is the mean cross-sectional area and d_1 and d_2 are the two end diameters of the truncated cone.

Correction for osmotic pressure

During an experiment different alkali concentrations develop in the different parts of the permeability cell. The concentration on the high-pressure side becomes different from that on the low-pressure side and both these concentrations may be different from the average concentration in the specimen. This gives rise to osmotic pressure. In recent work the permeability coefficient was calculated from the net pressure. That is, for Eq. (2),

$$\Delta h = \Delta h_a + \Delta h_o$$

where Δh_a = applied hydraulic head

Δh_o = hydraulic head due to osmosis

The head due to osmosis could be either positive or negative.

Most of the data reported in this paper are not corrected for osmotic pressure. The indications are that corrections would be small in most cases—not over 10 percent.

TEST RESULTS

Permeability of fresh paste

As shown by Steinour,⁹ fresh paste has structure and can be treated as a porous solid even before the cement sets. Under the force of gravity, the particles in cement paste settle, the rate of settlement being proportional to the permeability of the mass. It can be shown that the coefficient of permeability is directly proportional to the rate of bleeding. For the materials used in these tests, the proportionality constant is $1/2.15$.

The permeabilities of fresh pastes as calculated from measured bleeding rates are given in Table 1 for four different cements and one water-cement ratio. The bleeding rate data were published several years ago.¹⁰

These data indicate the order of magnitude of the permeabilities at a given water-cement ratio. The figures are to be compared later on with those for hardened paste. They show also that when the specific surfaces of the cements and the water-cement ratios of the pastes are equal, differences in permeability of fresh paste are not large, even though the cements differ considerably in chemical analysis.

Permeability of hardened paste

Effect of cement hydration—The chemical reactions between the constituents of portland cement and water progressively replace the original cement minerals with hydration products, principally cement gel. The volume of the cement gel (including gel pores) produced by hydrating the cement is approximately 2.3 times the volume of the cement. Consequently, the gel not only replaces the original cement minerals but also tends to fill the originally water-filled space. Table 2 shows the effects of these internal changes on the coefficient of permeability. The data pertain to a given paste at different stages of its hydration. Notice that within a week the coefficient of permeability dropped to about one one-hundred-thousandth of its initial value. By the 24th day it had dropped to less than a millionth of its initial value.

TABLE 1—PERMEABILITY OF FRESH PASTES

Cement* No.	Specific surface (Wagner)	W/C by weight	$K_1 \times 10^5$, cm per sec
15754	1800	0.5	56
15756	1800	0.5	63
15758	1800	0.5	51
15763	1800	0.5	84

*See Table 3 for compositions.

TABLE 2—REDUCTION OF PERMEABILITY BY CEMENT HYDRATION*

Age	Permeability coefficient K_1 , cm per sec
fresh	2×10^{-4}
5 days	4×10^{-8}
6 days	1×10^{-8}
8 days	4×10^{-9}
13 days	5×10^{-10}
24 days	1×10^{-10}
ultimate	0.6×10^{-10} (calculated)

*Cement No. 15754; specific surface = 1800 (Wagner); W/C = 0.7 by weight.

TABLE 3—REDUCTION OF PERMEABILITY BY CEMENT HYDRATION

Cement No.	Specific surface (Wagner)	W/C	K_1 , cm per sec	
			Fresh	Ultimate*
15754	1800	0.5	5.6×10^{-3}	4.4×10^{-12}
15756	1800	0.5	6.3×10^{-3}	5.2×10^{-12}
15758	1800	0.5	5.1×10^{-3}	5.7×10^{-12}
15763	1800	0.5	8.4×10^{-3}	6.3×10^{-12}

Computed potential compound compositions				
Cement	C_2S	C_2S	C_3A	C_4AF
15754	45.03	25.80	13.34	6.69
15756	48.51	27.90	4.63	12.60
15758	60.57	11.58	10.26	7.76
15763	28.33	57.52	2.22	5.96

*Approximate, by calculation.

Table 3 shows the total change in permeability for comparable pastes made with four different cements. The data in the fourth column are those given in Table 1. The fifth column gives approximately what the permeabilities would be after all the cement in the paste had become hydrated.

Effect of varying the cement content—The permeability of cement paste at a time when a given percentage of the cement has become hydrated is lower the higher the cement content of the paste. The relationship for a series of pastes in which about 93 percent of the cement was hydrated is given in Fig. 6A.

Fig. 6B gives data for specimens prepared from the same cement as in Fig. 6A, but for the specimens in Fig. 6B the cement had been treated in such a way as to induce false set. The cement was heated over night at 105 C so as to reduce the gypsum to the hemihydrate. The two curves show that at a given water-cement ratio (and at approximately the same

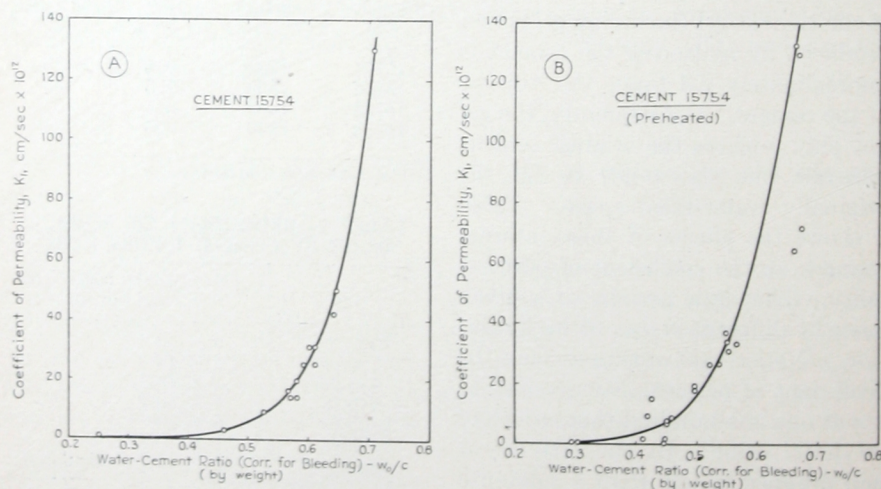


Fig. 6—Relationships between coefficient of permeability and water-cement ratio for mature paste

percentage of cement hydration) the coefficients for specimens made with the preheated cement were about double those for the other specimens.

We do not know whether or not there is any connection between the existence of false set and the slight increase in permeability. All we know is that the treatment that produced false set also increased the permeability coefficient.

Effect of chemical composition of the cement—In Table 3 the initial and final coefficients of permeability are shown for four cements having different chemical compositions. The figures for the ultimate coefficients are not direct test results but are values calculated from general relationships. The data are for pastes of one water-cement ratio; comparisons at other water-cement ratios give similar indications.

Influence of specific surface of cement—The cements used in this investigation were available at different degrees of fineness, the different grinds being made from the same clinker in a commercial plant. The permeabilities of pastes made with these cements are given in the fifth column of Table 4.

The figures in the last column, taken from the smooth curve drawn in Fig. 6B, may be used for comparison with the permeabilities of pastes made with cements of different fineness, and, with one exception, different chemical composition. The exception is the first item, cement No. 15364, which was made from the same clinker as cement No. 15754 represented in the last column.

TABLE 4—EFFECT OF DIFFERENCE IN CEMENT FINENESS ON PERMEABILITY OF HARDENED PASTE*

Cement lot No.	Specific surface (Wagner)	W./C by weight	Percent hydration	Permeability $K_1 \times 10^{15}$, cm per sec	Cement No. 15754; specific surface = 1900; percent hydration = 93; $K_1 \times 10^{15}$, cm per sec
15364	1040	0.54	79	25	30
		0.52	79	20	
		0.56	74	32	
		0.55	74	29	
		—	—	—	
15622	2200	0.54	76	26	75
		0.61	72	189	
		0.61	72	132	
		0.61	72	125	
		0.61	72	147	
15493	1470	0.61	72	148	82
		0.57	79	34	
		0.58	79	40	
		—	—	—	
		0.58	79	37	
15496	1740	0.60	88	34	67
		0.60	88	32	
		0.61	86	28	
		0.61	86	38	
		—	—	—	
15497	2500	0.60	87	33	75
		0.61	91	25	
		0.61	91	30	
		0.61	91	28	

*Cements preheated to reduce bleeding.

These data show that pastes having the same water-cement ratios are likely to have similar though not identical degrees of permeability after the cements have reached fairly advanced stages of hydration. The last three cements listed were all made from the same clinker and thus differed only in the degree of fineness. Even though the highest specific surface is nearly double the lowest, the coefficient of permeability of the finest is only about 25 percent less than that of the coarsest.

The first cement listed, No. 15364, may be compared directly with No. 15754 (sixth column). Here, although the degrees of hydration and the specific surfaces are considerably different, the coefficients of permeability are almost identical.

The pastes made with cement No. 15622, a Type II composition, appear to be somewhat more permeable than those made from the other cements. However, the difference may disappear at a later age, when the degrees of hydration would be more nearly equal. In general, the data indicate that a paste made from a coarsely ground cement may be just as impermeable as one made from a finer cement.

Effect of drying—All the data reported above are from tests on specimens kept wet continuously. To determine the effect of drying, two pairs of tests were made on the pastes that were partially dried after the curing period. One paste had been cured in the glass mold for 141 days and the other for 63 days. The pastes were then stored in closed glass vessels as follows:

First drying stage—208 days at 93 percent relative humidity

Second drying stage—1040 days at 79 percent relative humidity

Third stage—238 days at 100 percent relative humidity

Samples were shaped for permeability tests at the end of the second drying stage. During the two drying stages the specimens reached equilibrium with 79 percent humidity. In the third stage they returned to about 97 percent of saturation.*

By this procedure the moisture changes occurred gradually, and the stresses arising from differential shrinking or swelling were correspondingly low. Preliminary tests showed that drying a specimen rapidly by exposing it to a low humidity would crack it, or placing a dry specimen in water to resaturate it would produce stresses high enough to destroy the specimen.

TABLE 5—PERMEABILITY OF DRIED PASTES†

Ref. No.	W/C	Porosity of paste‡	Coefficient of permeability $\times 10^{12}$, cm per sec
L-4-A-A	0.50	0.410	990
L-4-A-B	0.50	0.412	915
L-27-A-A	0.50	0.408	400
L-27-A-B	0.50	0.404	1025

†Cement No. 15754 (preheated).

‡At time of test.

The permeabilities and porosities of two samples of each paste are given in Table 5. Three out of four specimens show permeability coefficients in the neighborhood of 1000×10^{-12} cm per sec. Other tests on comparable specimens (same porosities, same cement), but not subjected to drying and resaturating, gave coefficients

*The schedule used represented much more than the shortest periods needed for each stage.

TABLE 6—APPARENT EFFECT OF ALKALI CONTENT ON PERMEABILITY*

		Permeability K_1 , cm per sec, at		
		3 days	7 days	14 days
Leached	A	24.2×10^{-12}	24.6×10^{-12}	23.8×10^{-12}
	B	18.9×10^{-12}	20.0×10^{-12}	21.7×10^{-12}
Not leached	A	13.5×10^{-12}	15.5×10^{-12}	19.3×10^{-12}
	B	13.1×10^{-12}	14.5×10^{-12}	17.4×10^{-12}

*Cement No. 15761 — $Na_2O = 1.13$ percent; $K_2O = 0.44$ percent.

close to 15×10^{-12} . Thus, gradual drying to 79 percent relative humidity increased the coefficients of permeability about seventy-fold.

It is likely that the effect of drying on the coefficient of permeability would be greater than that indicated above if the specimens had been dried to equilibrium with a lower humidity. Specimens dried to various degrees are available but have not yet been tested.

From other data, we believe that the capillary space (as distinguished from gel pores) is in the form of isolated cavities, each cavity being surrounded by gel. We believe that shrinkage produced by drying may rupture some of the webs of gel between capillary cavities and thus increase the permeability. We found no evidence microscopically of cracks in the specimens.

Apparent effect of alkali content—Two sets of specimens from samples made with a high-alkali cement were prepared. One set was stored in limewater long enough to leach out most of its alkali, while the other set was kept in a saturated atmosphere. After the alkali had been removed from the one set, both sets were tested for permeability. The results are given in Table 6.

The leached specimens showed little or no change in permeability coefficient between the 3rd and 14th days that they were under test, whereas the unleached specimens showed a nearly 50 percent increase in coefficient of permeability. This might seem to indicate that when alkali is present in a specimen it lowers its permeability and that as the alkali is removed the permeability is increased. However, the indications are that after 3 days under test the alkali concentration in the water on the low-pressure side of the specimen was lower than it was in the water on the high-pressure side. Consequently, osmotic pressure counter to the applied pressure existed and reduced the rate of flow. As time went on, flow of water and diffusion of alkali tended to equalize the concentrations and thus reduce the osmotic pressure. As a consequence, more of the applied pressure became effective and the permeability coefficient apparently increased. Thus, these data do not indicate whether or not the alkali content of cement has any effect on the permeability of the paste made with that cement. The indications are that whatever the effect may be, it is small.

Comparison of hardened paste with rocks

Data on the permeabilities of various rocks are given in the first four columns of Table 7. Conical test samples were cut from selected pieces of

TABLE 7—PERMEABILITY OF ROCKS COMPARED WITH THAT OF HARDENED PASTE

Sample No.	Density, g per cc	Evaporable water capacity, g per cc of sample	K_1 , cm per sec	Mature paste of same permeability, W/C		Evaporable water capacity, g per cc of paste
				by weight	gal. per sack	
4	2.99	0.0057	3.45×10^{-13}	0.38	4.3	0.30
6	2.70	0.0082	9.20×10^{-13}	0.41	4.6	0.34
2	2.94	0.0065	1.15×10^{-12}	0.42	4.7	0.35
3	2.65	0.0018	1.26×10^{-12}	0.42	4.7	0.35
9	2.71	0.0046	1.72×10^{-12}	0.44	5.0	0.36
11	2.78	0.0180	3.34×10^{-12}	0.48	5.4	0.39
12	2.75	0.0310	8.05×10^{-11}	0.66	7.4	0.510
5	2.60	0.0140	1.15×10^{-10}	0.68	7.7	0.515
1	2.72	0.0510	2.30×10^{-10}	0.69	7.8	0.522
8	2.69	0.0073	7.48×10^{-10}	0.70	7.9	0.529
7	2.58	0.0430	1.72×10^{-9}	0.71	8.0	0.531
10	2.60	0.0052	2.18×10^{-9}	0.71	8.0	0.532

rock, tested for permeability, and then for total capacity for evaporable water.

The data are divided into two groups: (1) Rocks showing a coefficient of permeability less than 10^{-11} cm per sec. The capacity for evaporable water of all but one of these was less than 1 percent. (2) Rocks having coefficients of permeability greater than 10^{-11} cm per sec. In this group the capacities for evaporable water range from 0.5 to 5.0 percent. The fifth and sixth columns give the water-cement ratios of mature pastes that would have the same coefficients of permeability as the corresponding rock samples. The last column gives the capacities of the pastes for evaporable water. These comparisons show that the rock having the lowest degree of permeability was comparable with a mature cement paste of $W/C = 0.38$ by weight (4.3 gal. of water per sack of cement). For the rock of highest permeability the water-cement ratio of a comparable paste is about 0.71 (8 gal. of water per sack of cement).

Table 7A gives the source and description of the rock samples. The samples probably represented the rocks having minimum permeabilities, for they were selected pieces free from seams or visible imperfections. Data assembled by Ruettgers, Vidal, and Wing¹¹ indicate that when samples larger than ours were tested, permeability coefficients ranging several orders of magnitude higher than the highest shown in Table 7 were found.

TABLE 7A—DESCRIPTION OF SAMPLES

Sample No.	Lot No.	Source	Description
4	18278	Eau Claire, Wis.	Trap rock, dense, some crystal-boundary pores
6	18393A	C. H. Scholer	Marble, fine grained, dense
2	—	Phillips, Wis.	Quartz diorite, coarsely crystalline, crystal-boundary pores
3	18278	Eau Claire, Wis.	Quartz-feldspar, felsite, very dense
9	—	Thomaston, Me.	Limestone, crystalline
11	—	Elmhurst, Ill.	Limestone, crystalline; fine-grained marble
12	—	Elmhurst, Ill.	Limestone, crystalline; fine-grained marble
5	18278	Eau Claire, Wis.	Quartzite, imperfectly cemented; sandstone
1	—	Elgin, Ill.	Limestone, uniform, fairly dense, pure
8	18460	Santeeelah Dam	Granite, gray
7	18462	Raleigh County, W. Va.	Sandstone, porous
10	18200	Lithonia, Ga.	Granite

These data show that the pore size of a typical rock is much larger than the pore size of a comparable hardened cement paste. A rock having an evaporable water capacity of less than 0.005 g per cc may have a permeability coefficient equal to that of a paste having a water capacity of 0.35 g per cc.

SUMMARY OF TEST RESULTS

(1) The permeability coefficients of fresh paste, $W/C = 0.5$, range from 5×10^{-5} to 8×10^{-5} cm per sec for four cements having different chemical analyses but the same specific surface, 1800 Wagner. The permeability coefficient for $W/C = 0.7$ was 2×10^{-4} for the same cement that gave 0.6×10^{-4} at $W/C = 0.5$.

(2) The permeability of mature, hardened paste is between 1 millionth and one 10-millionth of that of fresh paste. It ranges from 0.1×10^{-12} to about 120×10^{-12} cm per sec for water-cement ratios ranging from 0.3 to 0.7 by weight.

(3) Mature, hardened pastes made with coarse-ground cements are no more permeable than those made with fine-ground cements when the pastes have equal total porosities. The indications are that they are slightly less permeable. However, the ultimate porosities of pastes made with coarse-ground cements are likely to be higher than those made with fine-ground cements if the initial water-cement ratios (corrected for bleeding) are equal.

(4) Pastes made with portland cements differing in chemical composition have similar permeabilities when the initial water-cement ratios (corrected for bleeding) are equal and when equal fractions of the different cements have become hydrated. At a given age and given water-cement ratio, pastes made with cements that hydrate slowly will have higher coefficients of permeability than those made with cements that hydrate rapidly.

(5) The foregoing conclusions pertain to the permeabilities of pastes that have never been allowed to dry. Drying increases the permeability. For the particular specimens reported here, drying at 79 percent relative humidity increased the permeability about seventy-fold.

(6) Samples of various rocks free from visible flaws had permeability coefficients ranging from 3×10^{-13} to 2×10^{-9} . This corresponds to the permeability coefficient of mature, hardened paste having a water-cement ratio 0.38 by weight at the low extreme and 0.7 by weight at the high extreme (4.3 and 8.0 gal. per sack, respectively).

ACKNOWLEDGMENT

We are indebted to Dr. L. S. Brown for the descriptions of rock samples given in Table 7A and to George Verbeck for selecting and shaping the rock samples used for permeability tests.

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